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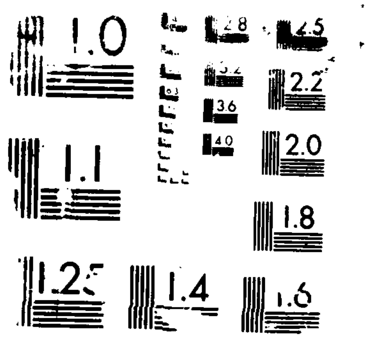
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Experimental noise spectra of beta alumina and Nasicon ceramics in contact with NaI propylene carbonate solution have been investigated. The noise of virgin contacts to both solid electrolytes decays exponentially with time. Low noise contacts can be established in a few hours. The current noise spectra show $f^{-3/2}$ and f^{-2} dependence in beta alumina and Nasicon, indicating bulk fluctuation arising from diffusion and reactions of the activated ions, respectively. Smaller correlation effects than in sodium beta alumina are observed which may be the result of the lower density of mobile sodium ions in the conducting lattice of both beta alumina and Nasicon.

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CONTACT AND CURRENT NOISE IN β ALUMINA AND NASICON CERAMICS

by

Chu Kun Kuo and James J. Brophy

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CONTACT AND CURRENT NOISE IN β ALUMINA AND NASICON CERAMICS

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Abstract

Experimental noise spectra of β alumina and Nasicon ceramics in contact with NaI propylene carbonate solution have been investigated. The noise of virgin contacts to both solid electrolytes decays exponentially with time. Low noise contacts can be established in a few hours. The current noise spectra show $f^{-3/2}$ and f^{-2} dependence in β alumina and Nasicon, indicating bulk fluctuation arising from diffusion and reactions of the activated ions, respectively. Smaller correlation effects than in sodium β"alumina are observed which may be the result of the lower density of mobile sodium ions in the conducting lattice of both β alumina and Nasicon.

INTRODUCTION

Conductivity fluctuation studies on sodium(1,2), silver(3), and lead(4) β"alumina have shown that the voltage fluctuations generated in the systems can be described as arising from bulk resistance,

diffusion and interfacial reaction noise. In most cases, the frequency dependence observed is in good agreement with standard noise expressions. Ionic correlation effects are suggested to account for the difference between the high experimental noise level observed and the concentration of mobile species derived from chemical composition[1,3,4]. This work extends the investigation into other sodium superionic conductors with the view of comparing and understanding the physical origins of noise in solid electrolyte. Beta alumina and Nasicon ceramics are used as samples. Both have comparably high ionic conductivity to sodium β"alumina.

EXPERIMENTAL PROCEDURES

Ceramic samples are obtained from Shanghai Institute of Ceramics, Shanghai, China. Their chemical compositions are:

Beta Alumina: Na_2O 8, MgO 2.5, Al_2O_3 89.5;

Nasicon: Na_2O 17.52, ZrO_2 46.45, SiO_2 22.65, P_2O_5 13.38

Square samples are cut from sintered ceramic pellets, polished with #500 carborundum paper, baked in air for three hours, and sealed into four plastic tubes containing 0.5 M NaI propylene carbonate solution to provide electrolyte and electrode contacts. Noise spectra are measured by using PAR 113 preamplifier with a digital FFT analyzer. The decay of contact noise in newly prepared cells is determined by the variation in noise levels at 1.0 Hz and 0.1 Hz with time.

Sampling for 10 FFT frames is completed within about 5 minutes. The temperature dependence of noise is determined at 5000 Hz and 10 Hz using an analogue measuring system.

CONTACT NOISE

NaI propylene carbonate solution yields stable contacts to β alumina after aging for several hours. The aged noise spectrum shows a relaxation noise at around 100 Hz as seen in some sodium β"alumina cells[1,5], which is assumed to reflect interfacial chemical noise. The aging time of Nasicon system is much shorter than that of β alumina and the noise level of aged Nasicon cells cannot be detected above the internal noise of the PAR 113 preamplifier below 10 Hz.

Similar to sodium β"alumina[6], the excess contact noise observed in virgin β alumina and Nasicon systems suggests a non-equilibrium reaction and the decay can be fitted to an exponential equation, Figure 1. The fitting equations are:

β alumina: $S(f,t)=A\exp(-0.0122t)$

$A=7.638\times10^{-15}$ at f=1 Hz; $A=2.51\times10^{-13}$ at f=0.1 Hz

Nasicon: $S(f,t)=A\exp(-0.0758t)$

$A=6.147\times10^{-15}$ at f=1 Hz; $A=2.462\times10^{-13}$ at f=0.1 Hz

If the time constant defined in the exponential equation is interpreted as a kinetic rate constant, we obtain k=0.0122/min for β alumina, 0.0199/min for β"alumina and 0.0758/min for Naiscon,

respectively. Thus the reaction rate increases in the sequence β alumina, β"alumina, Nasicon. From the similarity between the rate constants for β and β"alumina, as well as their structural similarity, it appears that the same chemical reaction is responsible for the contact noise.

CURRENT NOISE

Current noise is observed at both transverse and longitudinal electrodes when a constant dc current is passed between the longitudinal contacts. Figure 2 illustrates the transverse noise spectra of β alumina, showing $f^{-3/2}$ and I^2 dependence. Solid curves are calculated by the diffusion noise equation,

$$\frac{S(V,f,T)}{V^2} = \frac{2}{N}\left(\frac{2D}{L^2}\right)^{1/2} \omega^{-3/2}$$

by inserting the effective sample length L=0.8 cm, the diffusion coefficient $D=4\times10^{-7}$ cm^2/sec, the voltage across the sample V, and setting $N=4.5\times10^8$ ions (2.2×10^9 $ions/cm^3$). Interestingly, this calculation gives an effective concentration of mobile ions slightly higher than that of β"alumina[1], although according to the chemical composition more sodium ions are contained in the latter lattice. This suggests smaller mobile ion correlation effects in β alumina than in β"alumina.

Diffusion noise is not detected in the Nasicon cell. The current noise spectra, Figure 3, show f^{-2} behavior, suggesting chemical reac-

tion noise[1]. Longitudinal current noise spectra are similar to transverse noise, but the noise levels are greater. An unexpectedly high noise occurs as the current is increased to 330 μA. Moreover, high contact noise levels (i.e., I=0) are seen more than ten hours after current flow. Normally, post-current noise lasts only for about ten minutes. Both the high current noise and long-term post-current noise observed here can be attributed to a degradation reaction process in the bulk solid electrolyte. It is known that the Nasicon composition may be unstable in coexistence with metallic sodium[7-9]. Therefore, it is suggested that sodium deposited due to degradation may react with Nasicon during and after current flow and produce the excess reaction noise.

TEMPERATURE DEPENDENCE

It has been previously shown that the temperature dependence of the noise in β"alumina at high-and low-frequencies reflects thermal activation of the bulk resistance and diffusion or reaction noise, respectively[1,3]. Figure 4 illustrates experimental noise vs temperature plots for β alumina and Nasicon. The activation energy at 5000 Hz is 0.182 eV and 0.209 eV for β alumina and Nasicon, respectively, in agreement with values determined from conductivity data. The low frequency activation energy is more complicated since it measures variations in ionic correlations in the case of diffusion noise and the

degradation reactions of ionic species. Activation energies calculated from the 10 Hz data are 0.305eV and 0.503 eV for β alumina and Nasicon, both lower than that of sodium β"alumina, which is about 0.6 eV.

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* On leave from Shanghai Institute of Ceramics, Chinese Academy of Science.

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FIGURE CAPTIONS

Figure 1. Noise decay of β alumina and Nasicon in contact with NaI propylene carbonate solution.

Figure 2. Transverse current noise spectra in β alumina.

Figure 3. Transverse and longitudinal current noise spectra in Nasicon.

Figure 4. Temperature dependence of Nyquist and current noise of β alumina and Nasicon.

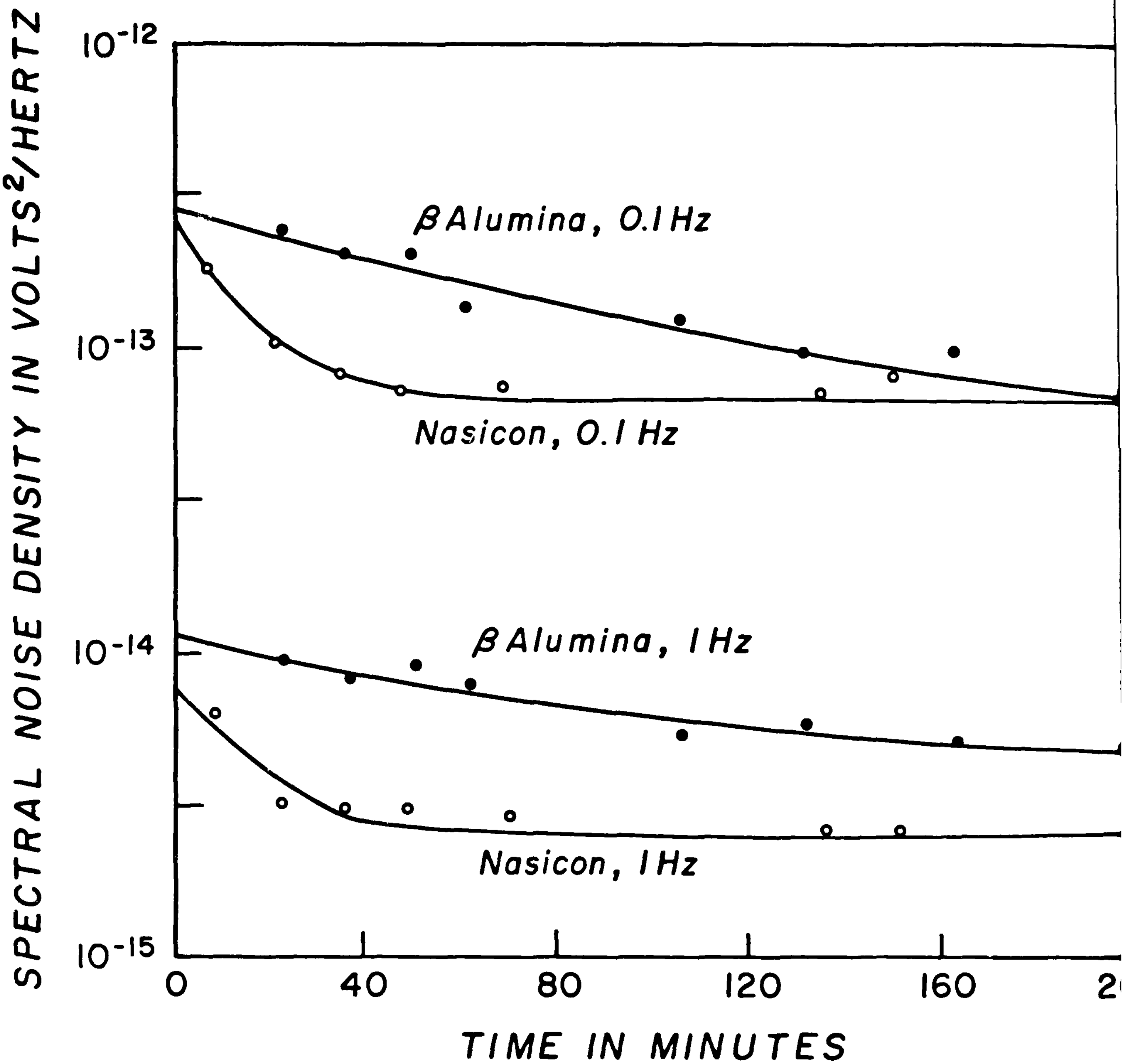
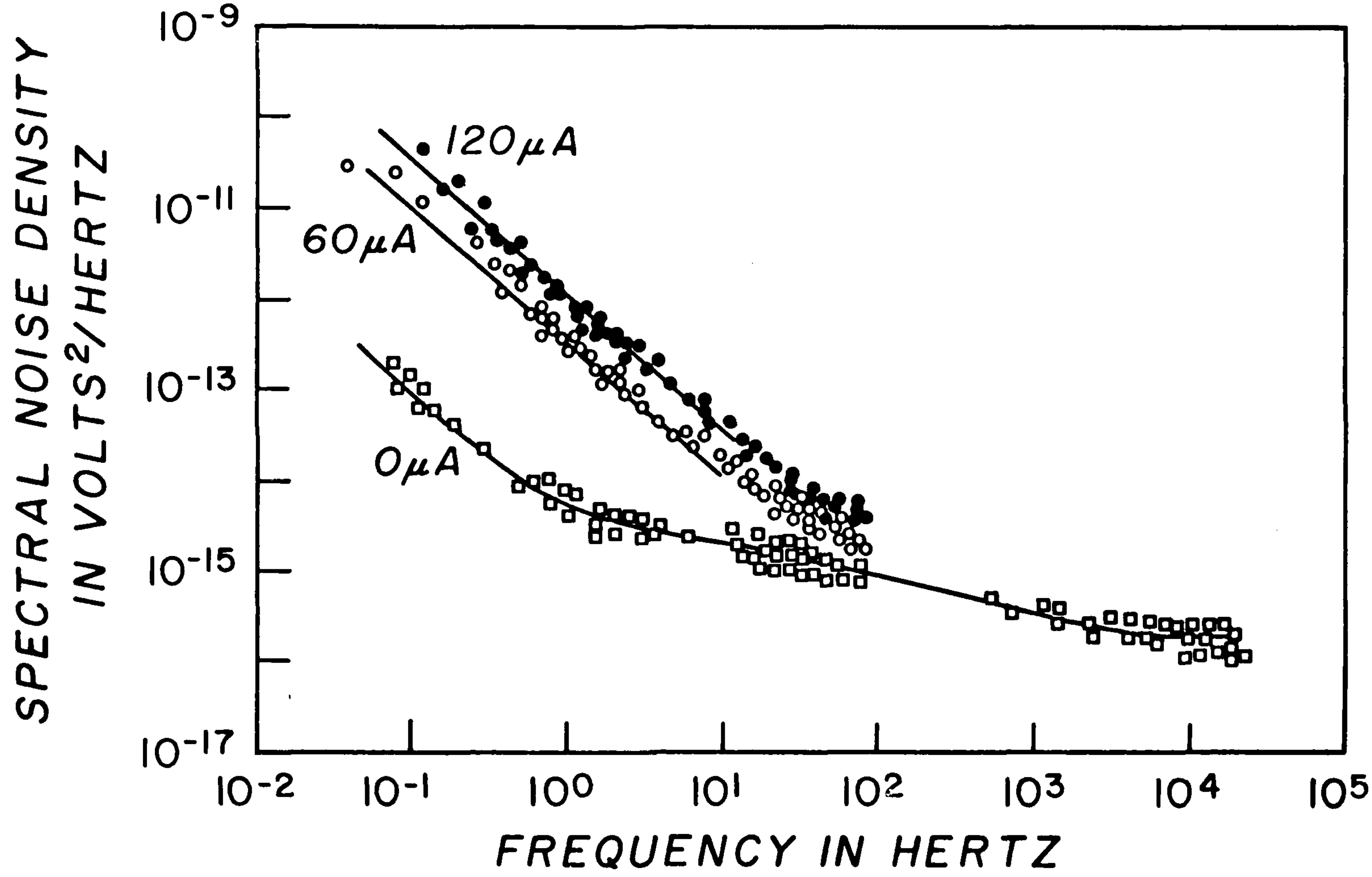
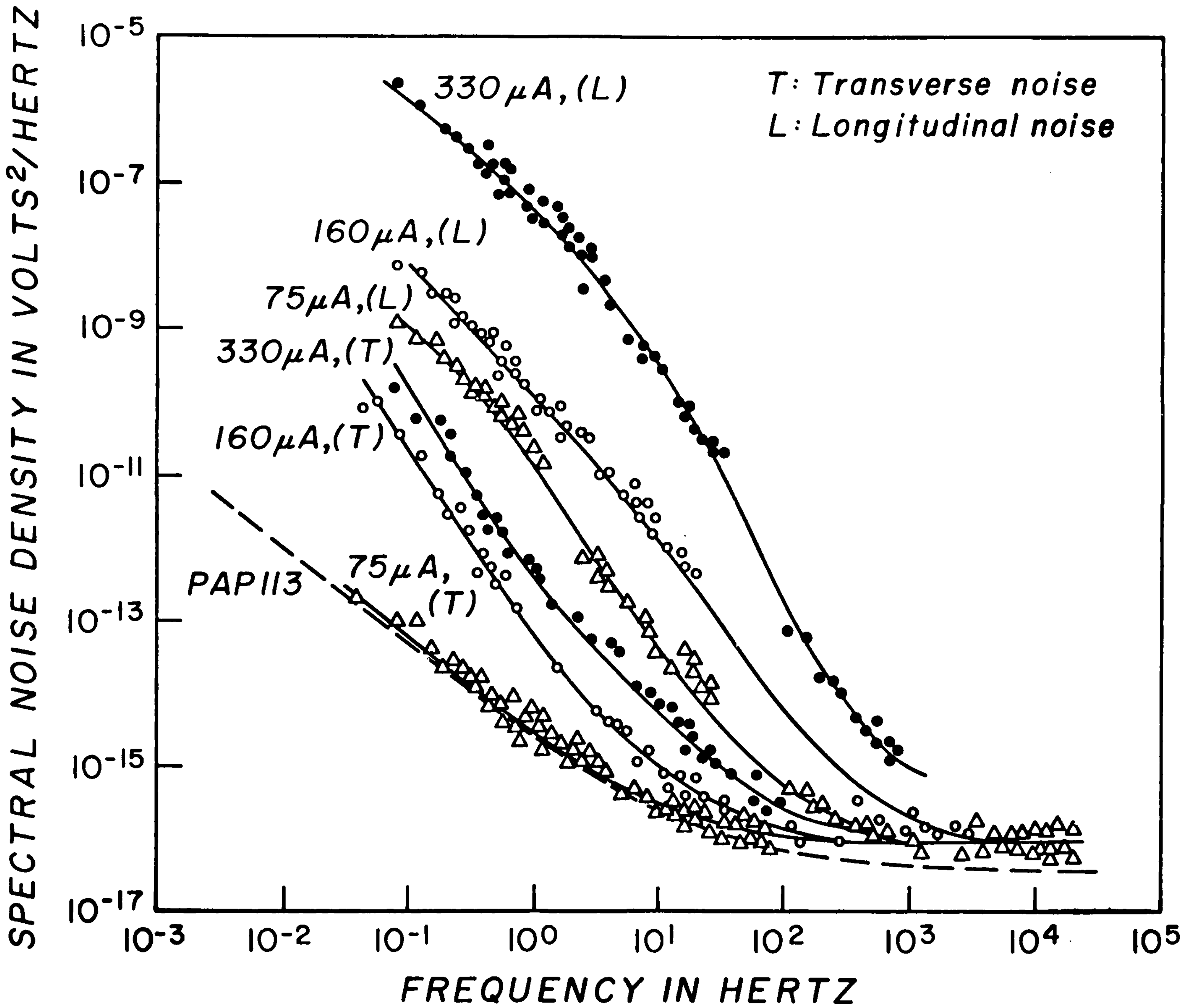

SPECTRAL NOISE DENSITY IN VOLTS²/HERTZ
10⁻¹²
10⁻¹³
10⁻¹⁴
10⁻¹⁵
β Alumina, 0.1 Hz
Nasicon, 0.1 Hz
β Alumina, 1 Hz
Nasicon, 1 Hz
0
40
80
120
160
TIME IN MINUTES

Figure 1.



SPECTRAL NOISE DENSITY IN VOLTS²/HERTZ
10-9
10-11
10-13
10-15
10-17
10-2
10-1
10⁰
10¹
10²
10³
10⁴
10⁵
FREQUENCY IN HERTZ
120μA
60μA
0μA

Figure 2.



330μA,(L)
T: Transverse noise
L: Longitudinal noise
160μA,(L)
75μA,(L)
330μA,(T)
160μA,(T)
75μA, (T)
PAP113
SPECTRAL NOISE DENSITY IN VOLTS²/HERTZ
FREQUENCY IN HERTZ

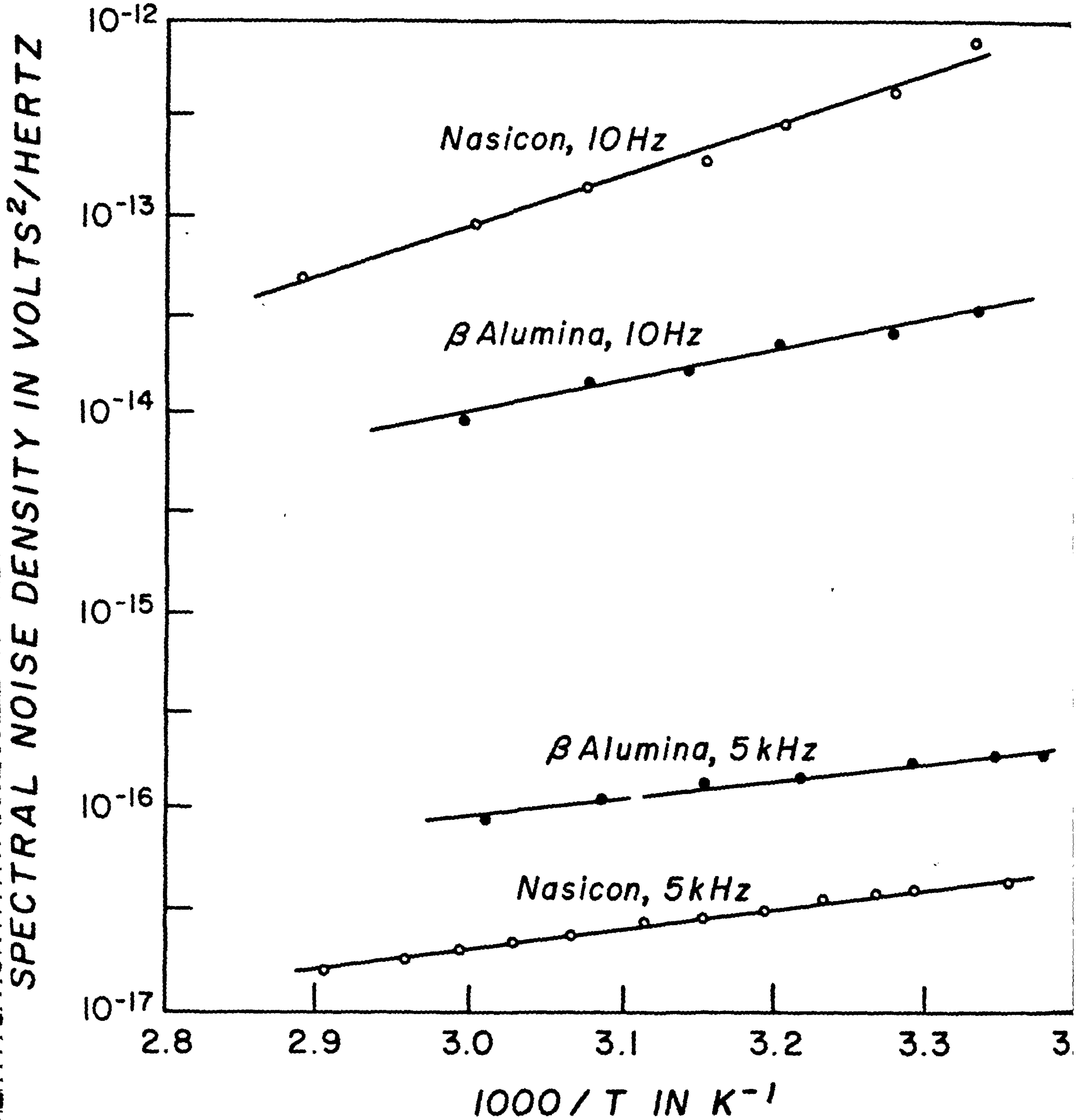

SPECTRAL NOISE DENSITY IN VOLTS²/HERTZ
10-12
10-13
10-14
10-15
10-16
10-17
Nasicon, 10 Hz
β Alumina, 10 Hz
β Alumina, 5 kHz
Nasicon, 5 kHz
2.8
2.9
3.0
3.1
3.2
3.3
1000/T IN K-1

Figure 4.

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